

REMARKS

I. Status

No claims have been amended in this paper. There is no issue of new matter.

Upon entry of this paper, claims 85-88, 90, 93, 95-100, 104-116, 135-137, and 141-175 are pending and subject to examination.

II. Claim rejections - 35 U.S.C. § 112

In the Advisory Action, the Office maintains the rejection of claims 85-88, 90, 93, 95-100, 104-116, 135-137, and 141-175 under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. The Office also maintains the rejection of claims 85-88, 90, 93, 95-100, 104-116, 135-137, and 141-175 are rejected under 35 U.S.C. § 112, first paragraph, as allegedly failing to comply with the enablement requirement. *See* Advisory Action at page 2. Specifically, the Office contends that the Tgi is not a constant, and that the corresponding pages of the Polymer Handbook, supporting Tgi is a constant, "is not provided in the reply nor elsewhere in the record and was not considered." *Id.* Applicants respectfully disagree and traverse this rejection for the following reasons as well as for the reasons of record.

Applicants maintain that Tgi as used in the present claims is theoretical and is a constant for a given monomer. Applicants hereby submit copies of the corresponding pages of the Polymer Handbook showing that Tgi is a constant for each particular monomer. For example, the Tgi for acrylic acid is 379 K (which is approximately 105.84 °C (379 K - 273.16)). Applicants note that, as shown on the attached copy of page VI 197, there are more than 10,000 papers containing data regarding glass

transition temperature, the attached copies of the corresponding pages of Polymer Handbook only representing a fraction of those data.

As such, the claims are not indefinite as would have been recognized by one of ordinary skill in the art. Accordingly, Applicants respectfully request that the rejection be withdrawn.

CONCLUSION


In view of the foregoing remarks, Applicants respectfully request reconsideration of this application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to Deposit Account No. 06-0916.

Respectfully submitted,

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POLYMER HANDBOOK

FOURTH EDITION

Editors

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Glass Transition Temperatures of Polymers

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mobility of the polymer chains, the molecules (long chains that have more than one crystallite) provide physical hindrance and increase T_g .

For polymer families, such as the methacrylates and polystyrenes, show high dependencies of T_g on intermolecular bonding can affect T_g either by increasing the cohesive energy of chain segments, or by increasing the backbone degrees of freedom of chain segments. This last concept has been used (1240) to aid in the development of models.

As crystallinity increases, polymer T_g 's may be little affected (51) or may increase (51,52) (at least for isothermal crystallization (53)) or may decrease (51,54). T_g values for polymers are the highest quoted on the sample with the lowest degree of crystallinity, other factors being equal.

The presence of crosslinks in a sample increases T_g relative to an uncrosslinked sample. This effect is independent of the chemical composition of the crosslinking agent, caused by the restricted motion of the segments near crosslinking sites. However, the crosslinking agent can behave similarly to a second solvent, inducing either an increase or a decrease in T_g due to a dilution effect.

The variation in published T_g data is caused by the nature of the samples. Common impurities are unpolymerized monomer, low molecular weight polymer, solvents, and plasticizers. Great care should be taken to remove such impurities. Their presence in small concentrations can lead to a decrease of 10–15°C in T_g of over 40°C and sometimes to the appearance of "diluent transitions", for example "water dilution" values are from publications that describe procedures taken to exclude diluents and the residual diluent in these diluents. Few references contain this information and most values should be regarded as only approximate.

Molecular Weight

T_g of a homopolymer generally increases with increasing molecular weight up to a limiting value, known as the persistent T_g value (48,104,105). The limiting value holds for polymers with particular end-groups and where crystallinity decreases with increasing molecular weight (107). For some polymers, T_g 's are independent of molecular weight (108).

For condensation polymers, are for polymers of rather low molecular weight and it seems likely that T_g values would be obtained if higher molecular weight samples were tested. Many polymers are not characterized with respect to molecular weight distributions. In the absence of molecular weight distributions, the only measure of molecular weight is a

value, which itself can be very dependent on polymer interactions and, to some extent on the temperature. Usually, the highest viscosities and the highest molecular weight polymers are associated with the most reliable data.

The classical model for the effect of molecular weight on T_g is (1219–1226)

$$T_g = T_g^\infty - \frac{A}{M_n}$$

This model suggests that the glass transition temperature reaches a limiting value when the number average molecular weight of the polymer is large. Cowie and Toporowski (1220) have shown that there is no further increase in T_g when the molecular weight is above a critical value, which is similar to the critical molecular weight for viscosity.

5. Thermal History

We have previously discussed in detail how thermal history (cooling rate, annealing time, and temperature), as well as the method of T_g measurement affects the reported T_g .

6. Pressure

Increasing pressure increases T_g in a linear relationship. A simple model is (Refs. 1227–1230)

$$T_g(p) = T_g(0) + sp$$

where $T_g(p)$ is the glass transition temperature as a function of pressure, p is pressure, and s is the linear pressure coefficient. This coefficient is 0.2 K/MPa for flexible aliphatic chains, and 0.55 K/MPa for semirigid aromatic chains (1231–1233). The effect of pressure on T_g can be important in some processing applications, such as injection molding. A different method for modeling the effect of temperature takes into account pVT data near T_g (1235–1237), giving an equation that includes the bulk modulus of the polymer glass.

D. ESTIMATION METHODS FOR THE GLASS TRANSITION TEMPERATURE

Several researchers have developed group contribution methods for correlating polymer properties, including the glass transition temperature (1238–1240). These techniques emphasize quantitative modeling of the various effects of polymer structure on T_g , and are a valuable aid to interpreting experimental data and estimating glass transition temperatures for new materials.

E. CLASSIFICATION, NOMENCLATURE, AND ABBREVIATIONS

Over 10000 papers contain glass transition data (43). This section of *Polymer Handbook* represents a fraction of these

data. Most of the data in the tables are for linear homopolymers. In general, the polymers contain no additives or diluents, and are thought to have low or no branching.

Polymers are subdivided into principle classes by the composition of their repeating chain segment: acyclic carbon polymers, carbocyclic polymers, acyclic heteroatom polymers, heterocyclic polymers, and copolymers. All entries are placed in the most senior class their structure commands (109,110) and appear in only one class. The subclasses and their entries are organized in alphabetical order.

1. Naming Conventions

With the exception of common polymers with accepted trivial names, the polymers are named substantially according to the ACS recommendations for polymer nomenclature (110) in conjunction with IUPAC rules (109); less common polymers are cross-referenced from the trivial to the systematic name. Systematic names are not given for all the polymers in order to save space. Substitutive nomenclature is generally used for simple radicals, but for long combinations of radicals replacement nomenclature has been used to provide a much shorter name (as for some fluorocrylates with ether side chains).

When sequences of radicals have repeated, the repeating sequence has been written once and prefixed "di", "tri", etc., as appropriate, for example, di(oxyethylene) for the sequence $-O-CH_2-CH_2-O-CH_2-CH_2-$. Note that the diradical "di(oxyethylene)" must be distinguished from the diradical "dioxethylene" which has the structure, $-O-O-CH_2-CH_2-$, and also the diradical "ethylenedioxy" which has the structure, $-O-CH_2-CH_2-O-$ (IUPAC rule C205.2). The principle underlying the last-named diradical has not generally been extended to the naming of polymers in this section, i.e., diradicals of structure $-X-Y-X-$ are not named YdiX, with the exception of alkanedioyl diradicals, because of the difficulty of locating indexed polymer names in which the diradicals are not named from left to right. Many polymers are derivatives of the diradical "propylene" $-CH(CH_3)-CH_2-$; the substituted diradical

"propylene" is used in naming polymers instead of "methylene" which could be preferred.

Polymer names are tabulated in alphabetical order within each subsection, but

1. prefixes like *sec-*, *tert-*, including designations and the numbers showing locations of substituents are ignored except as secondary and tertiary indicators in order. For example, poly(ethylene 2,6-naphthylidene) appears before poly(ethylene 1,4-terphenylidene) and poly(4-*p*-anisoylstyrene) appears before poly(4-*p*-toluylstyrene).
2. multiplying prefixes for various substituents, dimethyl or trimethyl, are observed in alphabetical order rather than being grouped together as in the 3rd edition of this Handbook.
3. the locations of substituents in otherwise identical polymers are taken as tertiary indicators of order. Numbers are arranged in increasing order at the point of difference. Thus, 2,3,8- comes before 2,3,9-.

Comments may include information as to the instrument used, and, whenever possible, information regarding the method of DSC measurement (e.g., heating rate, conditions of measurement, thermal history, and so on). Measurements were made as a function of a variable such as molecular weight (\bar{M}_w).

2. Abbreviations

HR	Heating rate
CR	Cooling rate
OCR	Zero cooling rate
Xp	Extrapolate
TH	Thermal history
DSC	Differential scanning calorimetry
TMA	Thermal mechanical analysis
DTA	Differential thermal analysis
DMA	Dynamic mechanical analysis
MW	Molecular weight
$f(\)$	Function of a variable
Mdpt	Midpoint
Intg	Integration

F. TABLES OF GLASS TRANSITION TEMPERATURES OF POLYMERS

TABLE 1. MAIN-CHAIN ACYCLIC CARBON POLYMERS

Polymer	CAS No.	T_g (K)	Remarks
1.1. POLY(ACRYLICS) AND POLY(METHACRYLICS)			
1.1.1. POLY(ACRYLIC ACID) AND POLY(ACRYLIC ACID ESTERS)			
Poly(acrylic acid)	9003-01-4	379	
Poly(1-adamantyl acrylate)		348	
Poly(adamantyl crotonate)		426	
Poly(adamantyl sorbate)		507	
Poly(benzyl acrylate)		388	
		279	

TABLE 1. *cont'd*

Polymer	CAS No.	T_g (K)	Remarks	Ref.
Poly(2-ethylbutyl acrylate)		223	Brittle point	421
→ Poly(2-ethylhexyl acrylate)	9003-77-4	223	Brittle point	422
Poly(ferrocenylethyl acrylate)	430		No experimental details	423
Poly(ferrocenylmethyl acrylate)	470-483		DSC heating rate	424
Poly(3-fluoroalkyl α -fluoroacrylate)	398			1261
Poly(4-fluoroalkyl α -fluoroacrylate)	368			1262
Poly(5-fluoroalkyl α -fluoroacrylate)	374			1263
Poly(8-fluoroalkyl α -fluoroacrylate)	338			1264
Poly(17-fluoroalkyl α -fluoroacrylate)	388			1265
Poly(fluoromethyl acrylate)	288		Estimated T_g	1266
Poly(furfuryl acrylate)	321			89
Poly(1H, 1H-heptafluorobutyl acrylate)	243			1278
Poly(5,5,6,6,7,7,7-heptafluoro-3-oxaheptyl acrylate)	228			155,846,427
Poly(2,2,3,3,5,5,5-heptafluoro-4-oxapentyl acrylate)	218			830,831
Poly(heptafluoro-2-propyl acrylate)	278-283		No details on sample or measurement	832
Poly(heptyl acrylate)	213		Brittle point	821,846
Poly(2-heptyl acrylate)	235		Brittle point	822
Poly(hexadecyl acrylate)	308		Brittle point	23,821,840,841
Poly(1H,1H,3H-hexafluorobutyl acrylate)	251			833
Poly(hexyl acrylate)	216		Brittle point	823
Poly(3-hydroxyalkanoate)	204			340
→ Poly(isobornyl acrylate) conventional syndiotactic isotactic	367			341
	369			842
→ Poly(isobutyl acrylate)	366			843
	249		Brittle point	83
	230			44
Poly(isopropyl acrylate) conventional syndiotactic isotactic	267-270			746,825,826
	271-284			827
	262			828
Poly(magnesium acrylate)	673		Estimated from copolymer data	84
Poly(3-methoxybutyl acrylate)	217			844
Poly(2-methoxycarbonylphenyl acrylate)	319			845
Poly(3-methoxycarbonylphenyl acrylate)	311			846
Poly(4-methoxycarbonylphenyl acrylate)	340			847
Poly(2-methoxyethyl acrylate)	223			848
Poly(4-methoxyphenyl acrylate)	324			849
Poly(3-methoxypropyl acrylate)	198			850
Poly(methyl acrylate) conventional	9003-21-8	283		18,22,23
	284		Dilatometer	189
	290			150
	282			1401,845
head to tail	278			576,720,775
head to head	304			821,834,838,840
				843,844
Poly(2-methylbutyl acrylate)	241		Brittle point	823,846
Poly(3-methylbutyl acrylate)	228		Brittle point	824
Poly(2-methyl-7-ethyl-4-undecyl acrylate)	253		Brittle point	825
Poly(2-methylpentyl acrylate)	235		Brittle point	826
Poly(2-naphthyl acrylate)	358			827
Poly(neopentyl acrylate)	295			746
Poly(1H,1H-nonafluoro-4-oxahexyl acrylate)	224			86
Poly(1H,1H-nonafluoropentyl acrylate)	236			86
Poly(nonyl acrylate)	215		Brittle point	86
	184			86
Poly(octyl acrylate)	25266-13-1	208	Brittle point	821,841
Poly(2-octyl acrylate)	228		Brittle point	828
Poly(1H,1H,5H-octafluoropentyl acrylate)	238			829
Poly(pentabromobenzyl acrylate)	453			830
Poly(pentachlorophenyl acrylate)	420			831
Poly(1H,1H-pentadecafluorooctyl acrylate)	256		Crystalline	832
Poly(1H,1H-pentafluoropropyl acrylate)	247			833
Poly(n-pentyl acrylate)	216			834

	CAS No.	T _g (K)	Remarks	Refs.
		331		1359
		330		1360
		344		1413
		359	with 25% wt. of chromophore I-doped polymer	1418
		378	with 25% wt. of chromophore II-doped polymer	1418
		348		1438
		347	DSC	1484
		285		824
		339		847
		298		746
		482	No experimental details	834
		~458-468	DSC heating rate	835
		355		1263
		353		1263
		350		1263
		320		1263
		310		1263
		347		1269
		336		1360
		~330		875
		258	Mechanical method	876
	25986-80-5	288	Brittle point, sample probably crystalline-may be T _m	821,866
	25087-17-6	268		695,846, 858,877, 1251,1443
		273		1401
			DSC	1484
		270		1416
		274		1413
	25249-16-5	328, 359	Conflicting data	746,878-880
		311	DSC, dry Xp	1098
		393	DSC, dry Xp	1199
		349		846,878
		358		1279
	64114-51-8	396/464/743 383		1401
		423		824
		326		1508
		281		746,821,824
		326		846,881
	9011-15-8	326		1401
		337		1438
		354		746,824,862
	26655-94-7	358		1401
		300		
		358		
		335	Heating rate: 20 K/min	842
		~763	Xp value	843
	54193-36-1	501	Xp data from plasticized samples	882
		379		746
	9003-21-8	273		1255
	9011-14-7			1102,1112,1101, 1107,1108
			DSC, onset, 16 deg/min HR, quenched, f(MW)	1101
			Dilatometer, CR 3 deg/h; creep relaxation, quenched	1109
		378		1432,1315, 1401,1288,1318